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COMBUSTION THEORY FOR LIQUIDS WITH A FREE SURFACE  
III. SPECIAL PROBLEMS

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16. Abstract  Two special problems concerning the combustion of liquids with a free surface, i.e., flame quenching during the mixing of a burning liquid inside a container and liquid burnout from a porous layer, are analyzed using a quasi-one-dimensional model. The critical parameters corresponding to the quenching of a burning fluid with a free surface are determined. Determinations are also made of the limiting pressure gradients corresponding to the transition from the combustion mode where the liquid evaporates from the surface of a porous layer to the mode where the phase transition surface lies inside the porous layer.			
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COMBUSTION THEORY FOR LIQUIDS WITH A FREE SURFACE  
III. SPECIAL PROBLEMS

S. N. Mil'kov, G. S. Sukhov, L. P. Yarin

The quasi-one-dimensional theory developed in [1,2] can be /3\*  
used to solve a broad group of problems related to combustion of liquids with a free surface. We will illustrate this with examples of approximate calculation of two processes which are interesting in terms of technical application: extinguishing a flame when a liquid in a container burns and when a liquid from a porous layer burns.

A flame above a free surface can be extinguished by rapid mixing [3]. The mechanism of this process involves the following. As the liquid is mixed, the free surface's temperature and, therefore, evaporation rate drop. If heat removal from the flame is nearly constant, the decrease in flow of vapor to the front reduces the reaction rate and, ultimately, results in extinction -- critical heat exchange conditions [4].

To find the values of parameters corresponding to extinction, we will use a one-dimensional model of a flame (fig. 1) and a quasi-heterogenous diagram of a flame front [5]. Let us write the equations for material and thermal balance at the front

$$G_{\phi-0} - G_{\phi+0} = W_{\phi}, \quad (1)$$

$$q(G_{\phi-0} - G_{\phi+0}) = Q_{\phi+0} - Q_{\phi-0}, \quad (2)$$

where  $G_{\phi-0}$  and  $G_{\phi+0}$  are, respectively, diffused flows of vapors approaching the flame front and departing from it;

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\*Numbers in the margin indicate pagination of the foreign text.

$Q_{\phi-0}$  and  $Q_{\phi+0}$ , thermal flows at the front;  $W_{\phi} = z\rho_1 c_{b\phi} \times$   
 $\times \exp(-E/RT_{\phi})$ , the rate of effective quasiheterogenous reaction.\*

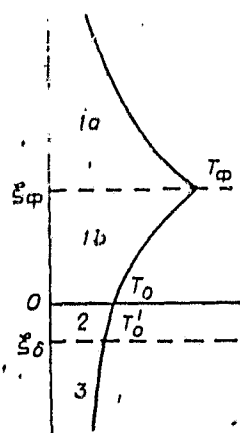


Fig. 1. Temperature distribution during combustion of a liquid with a free surface.  
 1a, b - Gas medium;  
 2 - Reacting liquid;  
 3 - Substrate.

Flows incorporated into equations (1) and (2) can be found by solving the system of quasi-one-dimensional transfer equations followed by calculation of the derivatives according to known temperature and concentration profiles [1]. To simplify the computations, in future approximation equations for diffusion and thermal flows we will use

$$G_{\phi-0} = -\rho_1 D \left( \frac{dc_b}{d\xi} \right)_{\phi-0} \approx \rho_1 D \frac{c_{b0} - c_{b\phi}}{\xi_{\phi}}, \quad (3) \quad \underline{4}$$

$$G_{\phi+0} = -\rho_1 D \left( \frac{dc_b}{d\xi} \right)_{\phi+0} \approx \rho_1 D \frac{c_{b\phi}}{\xi_0 - \xi_{\phi}}, \quad (4)$$

$$Q_{\phi+0} = \lambda_1 \left( \frac{dT_1}{d\xi} \right)_{\phi+0} \approx -\lambda_1 \frac{T_{\phi} - T_0}{\xi_{\phi}}, \quad (5)$$

$$Q_{\phi-0} = \lambda_1 \left( \frac{dT_1}{d\xi} \right)_{\phi-0} \approx \lambda_1 \frac{T_{\phi} - T_{1*}}{\xi_0 - \xi_{\phi}}, \quad (6)$$

$\xi_0$  is the nominal thickness of the layer of oxidizer above the free surface, at whose boundary  $c_a \approx c_{a\infty}$ .

Let us introduce the coefficient for vapor combustion

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\*The remaining values in (1) and (20) and subsequent equations, as well as subscripts, are taken from [1,2].

efficiency

$$\varphi = 1 - c_{b\phi}/c_{bm}, \quad (7)$$

where  $c_{b\phi} = c_{b0}(1 - \xi_\phi/\xi_0)$  is vapor concentration at section  $\xi = \xi_\phi$  if there is no combustion.

Substituting equations (3) and (4) into (1) with regard for (7) yields

$$\varphi = \frac{\tau}{\tau + c_{b\phi}^{1/\Theta_\phi}}, \quad (8)$$

$$\tau = z/D \cdot \xi_\phi(\xi_0 - \xi_\phi)/\xi_0; \quad \Theta_\phi = RT_\phi/E.$$

Considering  $\xi_0 \gg \xi_\phi$ , we obtain  $\tau \approx z\xi_\phi/D$ . Assuming that parameter  $\beta \approx \bar{\Omega}$ , during steady combustion until flame-out, we obtain an approximated equation for  $\xi_\phi$  [1].

$$\xi_\phi = \sqrt{\frac{\rho_1 D}{\alpha_c} \left( \frac{1 + \bar{\Omega}}{\bar{\Omega} - \beta} \right) \ln(1 + \bar{\Omega})}.$$

Where  $\beta = \bar{\Omega}c_{b0}$ ;  $\bar{\Omega} = \Omega/c_{a*}$ . Using this relationship and Clapeyron-Clausius' equation  $\beta = \bar{\Omega}\kappa \exp(-q_n/R/R_b E \Theta_\phi)$ , we express  $\tau$  as an exponential function of the free surface's temperature

$$\tau = \tau_0 [1 - \kappa \exp(-\bar{q}_n/\Theta_\phi)]^{-1/2}.$$

Here  $\tau_0 = z \left( \frac{\rho_1}{D\alpha_c} \frac{1 + \bar{\Omega}}{\bar{\Omega}} \right)^{1/2} \ln(1 + \bar{\Omega})$ ;  $\bar{q}_n = q_n R/ER_b$ .

Transforming (2) using (3)-(7), we obtain\*

$$\varphi_2 = \frac{(\Theta_\phi - \Theta_0) c_{p1} E}{c_{bm} q R}. \quad (9)$$

Since the scalar concentration of vapor  $c_{bm}$  is sufficiently

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\*In deriving (9), it was assumed that  $Le=1$ .

close to  $c_{b0}$ , we can, assuming that

$$c_{bm} \approx \kappa \exp(-\bar{q}_u/\theta_0), \quad (10)$$

give (9) the following form:

$$\varphi_2 = \frac{\theta_\phi - \theta_0}{\bar{q}} \exp(\bar{q}_u/\theta_0), \quad (11)$$

where  $\bar{q} = qR\kappa/c_{p1}E$ .

To determine the free surface's temperature  $\theta_0$ , one must use the equation for heat balance at the phase interface. Heat flow incorporated into these equations reflects both heat release from gas to liquid and transfer of heat by thermal conductivity and convection in the liquid. The solution to the problem includes calculation of transfer processes in the gas and liquid if there is forced convection (mixing) in the latter. However, to analyze the effect of mixing on the heat mode of combustion, there is no need to solve such a complicated problem. It can be limited merely to considering the relationship between combustion temperature (reaction rate) and free surface temperature, since physical considerations make it clear that mixing the liquid results in a reduction in  $\theta_0$ .

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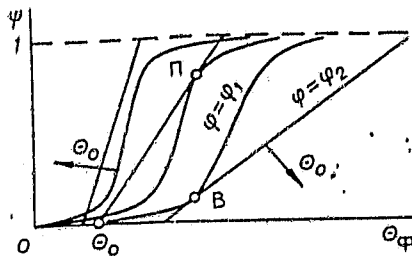


Fig. 2. - diagram  
( $\varphi_1$  is heat release,  
 $\varphi_2$  is heat removal).

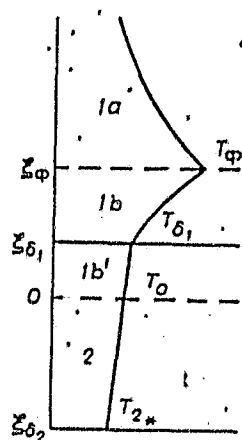


Fig. 3. Temperature distribution during combustion of a liquid from a porous layer.

1 - Gas phase; 2 - Porous substance (1b', region of vapor filtration through the porous layer).

Therefore, regarding  $\theta_0$  as a parameter, let us consider the path of curves  $\varphi_1(\theta_\phi)$  and  $\varphi_2(\theta_\phi)$  in variables  $\varphi-\theta$  (fig. 2). The function  $\varphi_2(\theta_\phi)$  is described by an S-curve starting at origin and, as  $\theta_\phi \rightarrow \infty$ , having an asymptote  $\varphi=1$ . Increasing  $\theta_0$  (accelerating mixing in the gas flame) shifts the curve  $\varphi_1(\theta_\phi)$  to origin. The function  $\varphi_2(\theta_\phi)$  is linear. A change in  $\theta_0$  shifts it along the x-axis and abruptly changes its slope. This reflects two consequences of the change in free surface temperature: a change in heat removal from the front, which is proportional to  $\theta_\phi - \theta_0$ , and vapor concentration at the phase interface, which is an exponential function of  $\theta_0$ . Figure 2 clearly shows that a reduction in  $\theta_0$  causes combustion temperature to drop and vapor concentration at the flame front to rise. At a certain critical  $\theta_0$ , curves  $\varphi_1(\theta_\phi)$  and  $\varphi_2(\theta_\phi)$  lose their common point at the upper temperature level, which corresponds to flame-out (point N).

Using (8) and (11), we will find the critical free surface temperature. Assuming that curves  $\varphi_1(\theta_\phi)$  and  $\varphi_2(\theta_\phi)$  are tangent, we derive an equation which relates critical combustion efficiency and critical temperature

$$\varphi_{np} = 1 - \frac{\theta_\phi^2}{\theta_\phi - \theta_0}. \quad (12)$$

Equating the right sides of (11) and (12), we find critical



temperature as a function of free surface temperature and adjusted calorific value  $\bar{q}$ :

$$\Theta_{np} = \frac{1}{2} \left\{ \frac{\bar{q} + 2\Theta_0 \exp\left(\frac{\bar{q}_n}{\Theta_0}\right)}{\bar{q} + \exp(\bar{q}_n/\Theta_0)} \pm \sqrt{\left[ \frac{\bar{q} + 2\Theta_0 \exp\left(\frac{\bar{q}_n}{\Theta_0}\right)}{\bar{q} + \exp(\bar{q}_n/\Theta_0)} \right]^2 - 4\Theta_0 \frac{\bar{q} + \Theta_0 \exp\left(\frac{\bar{q}_n}{\Theta_0}\right)}{\bar{q} + \exp\left(\frac{\bar{q}_n}{\Theta_0}\right)}} \right\}. \quad (13)$$

The minus sign before the radical in (13) represents /6  
combustion; the plus sign, extinction. From (8) and (11), we have

$$\frac{\tau(\Theta_0)}{\tau(\Theta_0) + e^{1/\Theta_0}} = \frac{1}{\bar{q}} (\Theta_0 - \Theta_0) \exp(\bar{q}_n/\Theta_0). \quad (14)$$

Equality (14) is valid for any steady state, including critical.

Solving the system of equations (13) and (14), one can find the critical free surface temperature  $\Theta_{0cr}$  as a function of assigned parameters  $\bar{q}$  and  $\bar{q}_n$ .

Let us consider the problem of combustion of a liquid from the porous layer of a substance. Experiments show that two different liquid combustion modes can be employed, depending on the system's hydraulic characteristics [6]. Given low porous layer hydraulic resistance (high medium porosity, low reacting liquid viscosity), the filtration supply mechanism meets the requirements of the reaction. Equilibrium is established in the system, and the evaporation front is localized at the layer's surface. If the medium's permeability diminishes, the equilibrium is disrupted, and the evaporation front shifts to within the layer. Its outer surface heats to a temperature above the liquid's boiling point. Therefore, the liquid- and gas-phase flow field can be divided into four typical zones (fig. 3). In the first, 2, the reactive liquid, exposed to

capillary forces and pressure applied from outside, is filtered through a layer of porous substance of thickness  $\xi_{\delta 2}$ . The liquid warms due to heat supplied to the porous substance from the flame front. In region lb', vapor formed during evaporation is filtered through a layer of porous substance of thickness  $\xi_{\delta 1}$ . In zones lb and la, the vapor mixes with the oxidizer found in the environment, and the components interact chemically.

In a quasi-one-dimensional approximation, diffusion combustion of a liquid filtered through a layer of porous substance is written as follows in a system related to the boiling front\*

$$\rho_1 u_1 \frac{dc}{d\xi} = \rho_1 D \frac{d^2 c}{d\xi^2} - \alpha_c \bar{c} \quad (15)$$

for the region  $\xi_{\delta 1} < \xi < +\infty$ ,

$$\rho_1 u_1 \frac{d\bar{c}}{d\xi} = \rho_1 D \frac{d^2 \bar{c}}{d\xi^2}, \quad (16)$$

$$\rho_1 u_1 c_{p1} \frac{dT'_1}{d\xi} = \lambda_1 \frac{d^2 T'_1}{d\xi^2}, \quad (17)$$

$$\frac{u'_1}{k_{\phi 1}} = - \frac{dp'}{d\xi}, \quad p' = \rho_1 \frac{R_b}{m} T' \quad (18)$$

for the region  $0 < \xi < \xi_{\delta 1}$ ,  $\pi$

$$m \rho_2 u_2 c_{p2} \frac{dT'_2}{d\xi} = \lambda_2 \frac{d^2 T'_2}{d\xi^2}, \quad (19)$$

$$\frac{u'_2}{k_{\phi 2}} = - \frac{dp}{d\xi} \quad (20)$$

for the region  $\xi_{\delta 2} < \xi < 0$ , where  $m$  and  $k_{\phi}$  are porosity and the

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\*At  $Le=1$ , one diffusion equation is sufficient to describe heat- and mass-transfer processes in the gas above the porous layer.

filtration factor;  $\lambda'_1$  and  $\lambda_2$ , effective coefficients of thermal conductivity for the filled porous medium in zones 1b' and 2.

Boundary conditions which are taken into account during integration of system (15)-(20) take the form

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$$\begin{aligned} \xi \rightarrow +\infty: T &\rightarrow T_{1*}, \quad \bar{c} \rightarrow 0, \\ \xi = \xi_\phi: T &= T_\phi, \quad \bar{c} = c_{a*}, \\ \xi = \xi_\delta: T &= T_\delta, \quad p = p_{1*}, \\ \xi = 0: T &= T_0, \quad \bar{c} = \bar{c}_0, \\ \xi = \xi_{\delta 2}: T &= T_{2*}, \quad p = p_{2*}. \end{aligned} \quad (21)$$

Balance equations reflecting the preservation of heat and substance flows toward typical surfaces should be added to conditions (21):

$$\xi = \xi_\phi, \quad \lambda_1 \left( \frac{dT_1}{d\xi} \right)_{\phi+0} - \lambda_1 \left( \frac{dT_1}{d\xi} \right)_{\phi-0} = q \rho_1 D \left( \frac{dc_b}{d\xi} \right)_{\phi-0}, \quad (22)$$

$$\xi = \xi_{\delta 1}, \quad \lambda_1 \left( \frac{dT_1}{d\xi} \right)_{\delta 1+0} = \lambda'_1 \left( \frac{dT'_1}{d\xi} \right)_{\delta 1-0}, \quad (23)$$

$$\xi = 0, \quad \lambda'_1 \left( \frac{dT'_1}{d\xi} \right)_{+0} - \lambda_2 \left( \frac{dT_2}{d\xi} \right)_{-0} = q_0 \rho_2 u_2 m, \quad (24)$$

$$\rho_1 u_1 c_{b0} - \rho_1 D \left( \frac{dc_b}{d\xi} \right)_0 = \rho_1 u_1 = \rho_2 u_2 m, \quad (25)$$

$$\beta = \bar{\Omega} \kappa \exp \left( -u \frac{\theta_n}{T_0/T_{1*}} \right). \quad (26)$$

However, without fully solving the problem, one can identify certain essential features of this process on the basis of the simplest possible model.\* For example, it is of practical

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\*Integrating system (15)-(20) does not involve any particular difficulties.

interest to evaluate limit pressure drop  $\Delta p_{np} = p_{2*} - p_{1*}$ , at which the evaporation front shifts inward into the porous layer. To find it, assuming  $T_\phi \gg T_{\delta 1}$ ,  $T_\phi = T_{K2}$ ,  $k_{\phi 1} \approx k_{\phi 2} = k_\phi$ ,  $\left(\frac{dT_1}{d\xi}\right)_{\delta 1+0} \approx T_\phi/\xi_\phi$ ,  $\left(\frac{dT_1}{d\xi}\right)_{\delta 1-0} \approx \frac{T_{\delta 1} - T_{K2}}{\xi_{\delta 1}}$ ,  $\left(\frac{dT_2}{d\xi}\right)_{\delta 1-0} \approx \frac{T_{K2} - T_{2*}}{h - \xi_{\delta 1}}$ ,  $\xi_\phi \gg \xi_{\delta 1}$  ( $h$  is the depth of the porous layer;  $T_{K2}$ , the liquid's boiling point), we obtain a system of three algebraic equations

$$\lambda_1 \frac{T_\phi}{\xi_\phi} = \lambda_1' \frac{T_{\delta 1} - T_{K2}}{\xi_{\delta 1}}, \quad (27)$$

$$\lambda_1' \frac{T_{\delta 1} - T_{K2}}{\xi_{\delta 1}} - \lambda_2 \frac{T_{K2} - T_{2*}}{h - \xi_{\delta 1}} = q_n \rho_2 u_2 m, \quad (28)$$

$$m \rho_2 u_2 = \frac{k_\phi \Delta p}{\xi_{\delta 1} / \rho_1 + \frac{h - \xi_{\delta 1}}{\rho_2}}, \quad (29)$$

which define  $T$ ,  $\xi_\delta$ , and  $u_2$  as a function of thermal, filtration, and geometric characteristics of the subject system. Specifically, solving (27)-(29) relative to  $\Delta p$ , we find

$$\Delta p = \frac{\xi_{\delta 1} (\rho_2 k_\phi = \rho_1) + \rho_1 h}{q_n \rho_1 \rho_2 k_\phi m} \left( \lambda_1 \frac{T_\phi}{\xi_\phi} - \lambda_2 \frac{T_{K2} - T_{2*}}{h - \xi_{\delta 1}} \right). \quad (30)$$

Introducing  $\xi_{\delta 1} = 0$  into (30), we obtain the desired equation, which relates limit values for parameters representing the transition of combustion from a mode in which the liquid evaporates from the porous material's surface to a mode where the surface of the phase transition lies within the porous substance layer

$$\Delta p_{np} = \frac{h}{q_n \rho_2 k_\phi m} \left( \lambda_1 \frac{T_\phi}{\xi_\phi} - \lambda_2 \frac{T_{K2} - T_{2*}}{h} \right). \quad (31)$$

Assuming that the layer of porous substance is sufficiently thick and the thermal effect of the chemical reaction is high ( $T_\phi/T_{1*} \approx \theta/\bar{\Omega}$ , a  $T_{K2} \approx T_{2*}$ ), we obtain the following

$$\Delta p_{np} = a_1 h / m k_\phi \xi_\phi \cdot \rho_{12} / \bar{\Omega} \cdot \theta / \theta_n, \quad (32)$$

where  $\rho_{12} = \rho_1 / \rho_2$ ;  $a_1 = \lambda_1 / c_{p1} \rho_1$ . Equation (32) shows that, all other

conditions being equal, the limit gradient is governed by the ratio of reaction heat to vapor-formation heat.

Using data from [6], we can approximate  $k_0 \Delta p_{sp}$ , which corresponds to the movement of the boiling front to the outer surface of the porous layer. For example, for kerosene in sodium chloride ( $h=120$  mm,  $d=16$  mm,  $m=0.4$ ), the transition from filtered combustion (boiling front within the layer) to free combustion (evaporation from the layer's surface) occurs when the grain cross section changes from 10 to 340 microns. The values  $k_0 \Delta p = 0.15 \cdot 10^{-2}$  and  $2.16 \cdot 10^{-5}$ , which correspond to these conditions, also determine the range of possible limit values  $k_0 \Delta p_{sp}$ . Calculation with (32) and data from [3] over the length of the flame yields  $k_0 \Delta p_{sp} = 0.09 \cdot 10^{-5} \text{ m}^2/\text{sec}$ , which is close to the lower limit of this range.

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